

1.084.448

PATENT SPECIFICATION

NO DRAWINGS

1.084.448



Date of Application and filing Complete Specification: Dec. 11, 1964.

No. 50476/64.

Application made in Switzerland (No. 15712) on Dec. 20, 1963.

Application made in Switzerland (No. 13202) on Oct. 12, 1964.

Complete Specification Published: Sept. 20, 1967.

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Index at acceptance:—C2 C(1E3K4, 1E3K6, 1E6K4, 1E6K6, 1E7A, 1E7B1, 1E7H2, 1E7N3, 3A4, 3A7V3A4, 1A7V3E1, 3A7V3L, 3A12A4C, 3A12B1, 3A12C5, 3A12C6)

Int. Cl.:—C 07 d 63/18

COMPLETE SPECIFICATION

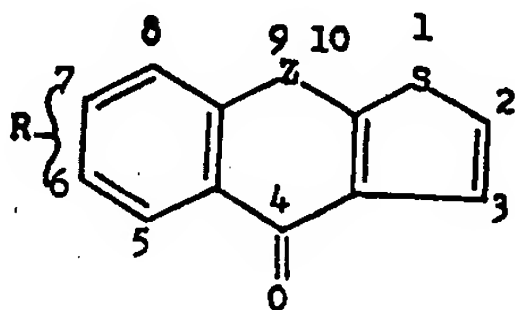
The inventors of this invention in the sense of being the devisers thereof within the meaning of Section 16 of the Patents Act 1949, are:— ERNST JUCKER, Steinweg 28, Ettingen, Switzerland; ANTON EBNÖTHER, Bruderholzstrasse 8, Reinach, Baselland, Switzerland; JEAN-MICHEL BASTIAN, Rheinparkstrasse 5, Birsfelden, Switzerland; ERWIN RISSI, Birsigstrasse 115, Basle, Switzerland, and ANDRE STOLL, Rheinparkstrasse 3, Birsfelden, Switzerland; all Swiss citizens.

Improvements in or relating to 4H-Benzo[4,5]Cyclohepta-[1,2-b]Thiophen-4-one Derivatives

We, SANDOZ LTD., of Lichtstrasse 35 Basle, Switzerland, a Swiss Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to new heterocyclic compounds and a process for their production.

The present invention provides 4H-benzo-[4,5]cyclohepta[1,2-b]thiophen - 4 - one derivatives of general formula I,



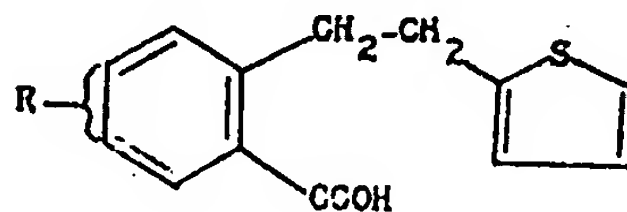
I

15 in which R signifies a chlorine or bromine atom or an alkoxy radical of 1 to 4 carbon atoms inclusive, and

20 Z signifies the radical
—CH=CH— or
—CH₂—CH₂—.

The present invention further provides a process for the production of compounds I, characterized in that a 2-[2-(2-thienyl)-

ethyl]-benzoic acid of general formula II, 25



II

in which R has the above significance, is cyclized by treatment with polyphosphoric acid and the resulting compound I in which Z signifies the radical —CH₂—CH₂— is dehydrogenated in the 9,10-position, when an unsaturated compound of formula I is required, by treatment with a halogenating agent followed by dehydrohalogenation. 30

One method of effecting the process of the invention consists in that a 2-[2-(2-thienyl)-ethyl]-benzoic acid substituted in the 4- or 5-position by a chlorine or bromine atom or an alkoxy radical of 1—4 carbon atoms inclusive, is heated with polyphosphoric acid to 70 to 150° for 30 minutes to 3 hours. The reaction mixture is subsequently poured into ice water, the solution is filtered and then extracted with an inert organic solvent, e.g. methylene chloride or diethyl ether. Compound I in which Z signifies the radical —CH₂—CH₂— is isolated in known manner and purified by distillation in a high vacuum and subsequent crystallization. 40 45

Compounds I in which Z signifies the radical —CH=CH— are obtained from the above described 9,10-dihydro-4H-benzo[4,5]cyclo- 50

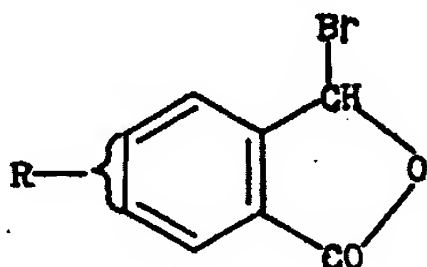
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hepta[1,2-b]thiophen-4-one derivatives as follows: The 9,10-dihydro derivative is treated with a brominating or other halogenating agent and the brominated compound is subsequently heated with an organic base in order to split off hydrogen bromide or other hydrogen halide.

It is especially advantageous to use the following process for the dehydrogenation: 9,10-dihydro-4H-benzo[4,5]cyclohepta[1,2-b]thiophen-4-one derivative is heated for a number of hours with N-bromosuccinimide in absolute carbon tetrachloride in the presence of a catalytical amount of dibenzoyl peroxide. The resulting reaction mixture is then filtered, the filtrate is evaporated to dryness, the residue is dissolved in a trialkylamine, preferably trimethyl or triethylamine and the solution is heated. The dehydrogenated final product ($Z = -CH=CH-$) is isolated in known manner and purified by crystallization.

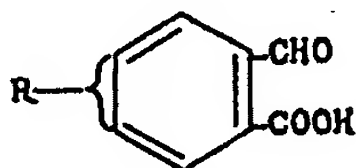
The following method is suitable for the production of the 2-[2-(2-thienyl)-ethyl]-benzoic acid derivatives II used as starting material:

An o-phthalide substituted in the 5- or 6-position by a chlorine or bromine atom or an alkoxy radical of 1-4 carbon atoms inclusive, is heated for a number of hours in an inert organic solvent, preferably carbon tetrachloride, together with N-bromosuccinimide in the presence of a catalytical amount of dibenzoyl peroxide and the resulting 3-bromophthalide derivative of general formula III,



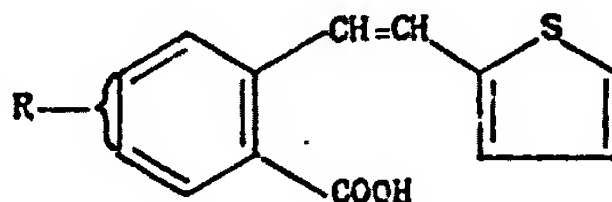
III

in which R has the above significance, is heated with water, whereby the corresponding phthalaldehydic acid derivative of formula IV,



IV

in which R has the above significance, results. The phthalaldehydic acid derivative is then condensed in a suitable anhydrous organic solvent and in the presence of an alkaline condensation agent with 2-thienyl-diethylphosphonate and the resulting 2-[2-(2-thienyl)-vinyl]-benzoic acid derivative of formula V,

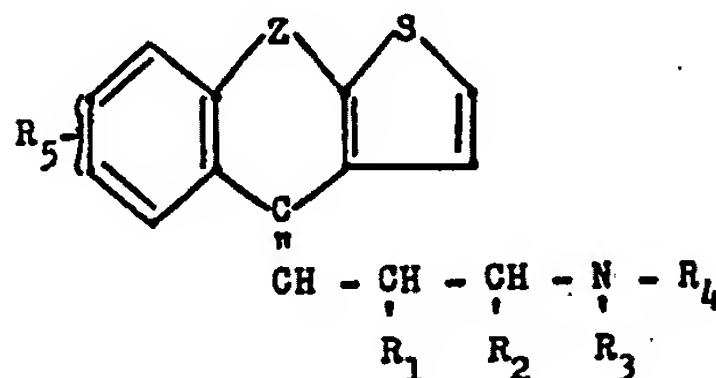


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V,

in which R has the above significance, is reduced to the 2-[2-(2-thienyl)-ethyl]-benzoic acid derivative II. Sodium amalgam in aqueous alcohol or hydrogen iodide and red phosphorus in glacial acetic acid may, for example, be used as reducing agent.

Compounds of formula I are useful as intermediate compounds, for example, for the production of compounds of the formula



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in which R_5 signifies a chlorine or bromine atom or an alkoxy radical of 1 to 4 carbon atoms inclusive,

Z signifies the radical

$-CH=CH-$ or
or $-CH_2-CH_2-$,

EITHER

each of R_1 and R_2 signifies a hydrogen atom or a methyl, with the proviso that R_1 and R_2 may be similar,

each of R_3 and R_4 signifies an alkyl radical of 1 to 4 carbon atoms inclusive with the proviso that R_3 and R_4 may be similar, or both together with the nitrogen atom linking them signify the pyrrolidino, piperidino, piperazino, 4-methyl-piperazino or a 4-hydroxy-alkyl (C_2-C_3)-piperazino radical,

OR

R_1 signifies an alkyl radical of 1 to 4 carbon atoms inclusive, and either

R_3 and R_4 together signify the dimethylene or trimethylene radical, and

R_2 signifies a hydrogen atom, or

R_3 and R_4 together signify the trimethylene or tetramethylene radical, and

R_1 signifies a hydrogen atom, which are described and claimed in our Patent Specification No. 1,084,450 (Applica-

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tion No: 50551/64); the use of these compounds is set forth in said copending specification.

In the following non-limitative Examples all temperatures are indicated in degrees Centigrade. The melting and boiling points are uncorrected.

EXAMPLE 1:

6 - chloro - 9,10 - dihydro - 4H - benzo[4,5]cyclohepta[1,2-b]thiophen - 4 - one.

90 cc of 84% phosphoric acid and 126 g of phosphorus pentoxide are first stirred at 125—130° for 30 minutes. 30 g of finely powdered 5-chloro-2-[2-(2-thienyl)-ethyl]-benzoic acid are added at the same temperature during the course of 30 minutes. The reaction mixture is stirred for a further hour at 125—130°, poured into 1500 cc of ice water, the solution is filtered through highly purified diatomaceous earth and extracted three times with methylene chloride. The organic phase is washed with 2N sodium carbonate solution, then with water, dried over magnesium sulphate, the solvent is evaporated and the residue distilled in a high vacuum, whereby 6-chloro-9,10-dihydro-4H - benzo[4,5]cyclohepta[1,2-b]thiophen-4-one distils over as an oil at 185—195°/0.1 mm Hg and crystallizes. Melting point 107—108° from ether.

The 5 - chloro - 2 - [2 - (2 - thienyl)-ethyl] - benzoic acid used as starting material is produced as follows:

5-chloro-phthalaldehydic acid.

A mixture of 60 g of 6-chlorophthalide, 61.5 g of N-bromosuccinimide and 0.15 g of benzoyl peroxide in 4000 cc of anhydrous carbon tetrachloride is heated to the boil for 22 hours whilst stirring. The hot solution is filtered and the filtrate is evaporated at 15 mm Hg. The crude 3-bromo-6-chlorophthalide is then heated to 100° together with 400 cc of water for 8 hours and the solution is filtered through highly purified diatomaceous earth. After cooling the precipitated acid is filtered off, the diatomaceous earth is heated to the boil once more together with the mother liquor for a number of hours, the solution is filtered whilst hot and evaporated to a small extent at reduced pressure, whereby a further portion of acid is obtained. After drying in a vacuum at 90° the acid melts at 136—138°.

5 - chloro - 2 - [2 - (2 - thienyl) - vinyl] - benzoic acid.

1 to 2 cc of a solution of 70 g of 5-chlorophthalaldehydic acid and 89 g of 2-thienyl-diethyl-phosphonate in 135 cc of dimethyl formamide are added dropwise to a suspension of 45.6 g of sodium methylate in 135 cc of dimethyl formamide, whereby the tem-

perature of the mixture rises to 35—40°. The flask is then placed on an ice bath and the entire solution of 5-chloro-phthalaldehydic acid and 2-thienyl-diethyl-phosphonate is added dropwise as rapidly as possible so that the internal temperature remains at 35—40°. The reaction mixture is then stirred at room temperature for a further 30 minutes. 4300 cc of water are slowly added to the reaction solution at 10—15° whilst cooling well and the aqueous solution is shaken out with 300 cc of benzene. The aqueous solution is then carefully adjusted to a pH value of 3 to 4 with 2N hydrochloric acid at 10—15°. After a number of hours the precipitated acid is filtered off and dried. Melting point 152—153° from benzene.

5 - chloro - 2 - [2 - (2 - thienyl) - ethyl] - benzoic acid.

18.8 g of sodium are melted with anhydrous toluene, whereupon 1250 g of pure mercury are added dropwise whilst shaking frequently at such a rate that the toluene boils. The mixture is then heated to 120—140° whilst stirring and as soon as all the toluene is distilled off cooling is effected to 60°. A solution of 50 g of 5-chloro-2-[2-(2-thienyl)-vinyl]-benzoic acid in 350 cc of 95% ethanol is poured into the homogeneous amalgam and the mixture is vigorously stirred for 1½ to 2 hours. The mercury is then separated, washing is effected three times with ethanol and the combined ethanolic solutions are diluted with 5000 cc of water. The solution is filtered through highly purified diatomaceous earth and slowly adjusted to a pH value of 1 with 2N hydrochloric acid whilst stirring and cooling. After a number of hours the precipitated acid is filtered off and recrystallized from ethanol. Melting point 134—135°.

EXAMPLE 2:

7 - chloro - 9,10 - dihydro - 4H - benzo[4,5]cyclohepta[1,2-b]thiophen - 4 - one.

104 g of phosphorus pentoxide and 74 cc of 80% phosphoric acid are mixed and the mixture is heated to 140° for 30 minutes whilst stirring. 25.7 g of 4-chloro-2-[2-(2-thienyl)-ethyl]-benzoic acid are then added at the same temperature and stirring is effected for a further 3 hours at 140°. The hot reaction mixture is then poured into 1400 cc of water. Extraction is effected a number of times with ether, the combined extracts are dried over sodium sulphate and the solvent is evaporated at 30° and reduced pressure. The viscous residue is distilled in a hot air bath at a strongly reduced pressure. Boiling point 170—180°/0.1 mm Hg. The distillate is made to crystallize in a mixture of ether and petroleum ether. Pure 7-chloro-9,10 - dihydro - 4H - benzo[4,5] cyclohepta

[1,2-b]thiophen - 4 - one melts at 63—64°.

The 4 - chloro - 2 - [2 - (2 - thienyl)-ethyl] - benzoic acid used as starting material is produced as follows:

5 3 - bromo - 5 - chloro - phthalide.

A mixture of 72.5 g of 5-chloro-phthalide, 76.6 g of N-bromosuccinimide and 0.25 g of dibenzoyl peroxide is heated to the boil in 4300 cc of absolute carbon tetrachloride whilst stirring for 22 hours. After cooling the reaction mixture is filtered and the filtrate evaporated to dryness at 50° and reduced pressure. Pure 3-bromo-5-chloro-phthalide, having a melting point of 108—110°, is obtained from the crystalline residue after recrystallization from acetone.

4 - chloro - phthalaldehydic acid.

59.1 g of 3-bromo-5-chloro-phthalide are suspended in 600 cc of water and the suspension is heated to 100° whilst stirring well for 8 hours. Cooling is then effected to 0°, the 4-chloro-phthalaldehydic acid is filtered off and washed with ice cold water until neutral. Pure 4-chloro-phthalaldehydic acid, having a melting point of 184—186°, is obtained without further purification.

4 - chloro - 4 - [2 - (2 - thienyl) - vinyl] - benzoic acid.

A solution of the mixture of 36.9 g of 4-chloro-phthalaldehydic acid and 47.0 g of 2-thienyl-diethyl-phosphonate in 130 cc of dimethyl formamide is added dropwise whilst stirring well to a suspension of dry sodium methylate produced from 10.4 g of sodium in 110 cc of dimethyl formamide. The dropwise addition is effected at such a rate that the internal temperature always amounts to 35—45°. Stirring is subsequently effected for a further 15 minutes at room temperature and the mixture is then poured into 6000 cc of water. The alkaline aqueous solution is carefully acidified to a pH value of 3 with dilute hydrochloric acid. The precipitated substance is filtered off and after recrystallization of the crude product from ethanol pure 4 - chloro - 2 - [2 - (2 - thienyl)-vinyl] - benzoic acid, having a melting point of 198—200°, is obtained.

4 - chloro - 2 - [2 - (2 - thienyl) - ethyl] - benzoic acid.

A suspension of 18.5 g of 4-chloro-2-[2-(2-thienyl)-vinyl]-benzoic acid in 350 cc of 95% ethanol is added at once at 50° to sodium amalgam produced from 7.0 g of sodium and 520 g of mercury. Stirring is then effected for 3 hours at room temperature and the ethanolic solution of the reaction product is then separated from the mercury. Evaporation to dryness is effected at 60° and reduced pressure and the residue is dissolved in 1000 cc of water. The solution is filtered

and the filtrate acidified with concentrated hydrochloric acid. The reaction product is extracted with ether, the extracts are dried over sodium sulphate and the solvent is evaporated at 30° and reduced pressure. The crystalline residue is recrystallized from ethanol and yields pure 4-chloro-2-[2-(2-thienyl)-ethyl]-benzoic acid having a melting point of 127—128°.

EXAMPLE 3:

6 - bromo - 9,10 - dihydro - 4H - benzo[4,5]cyclohepta[1,2-b]thiophen - 4 - one.

A mixture of 100 cc of 84% phosphoric acid and 140 g of phosphorus pentoxide is first stirred at 125—130° for 30 minutes. 30 g of 5-bromo-2-[2-(2-thienyl)-ethyl]-benzoic acid are then added portionwise at the same temperature during the course of 30 minutes. The mixture is then stirred for a further 45 minutes at the same temperature, cooled to 70° and poured into 1500 cc of ice water whilst stirring. The reaction product is then extracted three times with methylene chloride, the combined methylene chloride extracts are washed three times with 2N sodium carbonate solution and twice with water, dried over sodium carbonate and the solvent is evaporated at 15 mm Hg. The oily residue is distilled in a high vacuum, whereby 6 - bromo - 9,10 - dihydro - 4H - benzo[4,5]cyclohepta[1,2-b]thiophen - 4 - one distils over at 200—220°/2—3 mm Hg.

The brown distillate is then dissolved in ether, the ethereal solution is diluted with 30 cc of ethanol, filtered through active charcoal and the ether is evaporated. The ethanolic solution is left to cool slowly and the greenish ketone, having a melting point of 88—90°, is filtered off. After recrystallization from ethanol the ketone melts at 93—94.5°.

The 5 - bromo - 2 - [2 - (2 - thienyl)-ethyl] - benzoic acid used as starting material is produced as follows:

5-bromo-phthalaldehydic acid.

A mixture of 1000.0 g of 6-bromophthalide, 81.0 g of N-bromosuccinimide and 0.2 g of dibenzoyl peroxide in 6000 cc of anhydrous carbon tetrachloride is heated to the boil for 22 hours whilst stirring. The solution is filtered whilst hot and the solvent is evaporated at 15 mm Hg. The crude 3,6-dibromophthalide is then heated at reflux for 4 hours together with 2500 cc of water, the resulting hot solution is filtered through highly purified diatomaceous earth, the filtrate is cooled and the precipitated acid filtered off. After concentrating the mother liquor to 500 cc a further portion of acid is separated. After drying in a high vacuum at 60° 5-bromophthalaldehydic acid melts at 136—138°.

5 - bromo - 2 - [2 - (2 - thienyl) - vinyl] - benzoic acid.

1 to 2 cc of a solution of 52.0 g of 5-bromo-phthalaldehydic acid and 53.4 g of 2-thienyl-diethyl-phosphonate in 80 cc of dimethyl formamide are added dropwise to a suspension of 27.4 g of sodium methylate in 100 cc of dimethyl formamide, whereby the temperature of the mixture rises to 35°. The flask is then placed in an ice bath and the entire solution of 5-bromo-phthalaldehydic acid and 2-thienyl-diethyl-phosphonate is added dropwise as rapidly as possible at such a rate that the internal temperature remains at 34—40°. The mixture is then stirred for a further 30 minutes at room temperature. 2500 cc of water are added to the reaction solution at 10—15° whilst cooling and the aqueous alkaline solution is shaken out once with 150 cc of benzene. The aqueous solution is then carefully adjusted to a pH value of 3.5 at 5—10° with 2N hydrochloric acid. After a number of hours the precipitated acid is filtered off and recrystallized from benzene/ethanol. Melting point 174—175°.

5 - bromo - 2 - [2 - (2 - thienyl) - ethyl] - benzoic acid.

A solution of 40.0 g of 5-bromo-2-[2-(2-thienyl)-vinyl]-benzoic acid in 800 cc of glacial acetic acid is heated to 75°. 40.0 g of red phosphorus and 220 cc of 56% hydriodic acid are added at the same temperature and heating to the boil is subsequently effected for 10 minutes whilst stirring. The hot reaction mixture is then filtered through highly purified diatomaceous earth and the filtrate is slowly poured into 4000 cc of water and ice. The aqueous portion is decanted and the viscous residue is rubbed with fresh water. The solid product is then separated and dissolved in 600 cc of benzene, the benzene solution is dried over sodium sulphate and the filtrate concentrated and cooled. After drying at 15 mm Hg and a temperature of 80° the precipitated acid melts at 122—124°.

EXAMPLE 4:

6 - methoxy - 9,10 - dihydro - 4H - benzo[4,5]cyclohepta[1,2-b]thiophen - 4 - one.

A mixture of 80 cc of 84% phosphoric acid and 112 g of phosphorus pentoxide is first stirred at 125—130° for 30 minutes. The resulting polyphosphoric acid is then cooled to 90° and covered with a layer of 250 cc of anhydrous toluene. A solution of 22.0 g of 5-methoxy-2-[2-(2-thienyl)-ethyl]-benzoic acid in 100 cc of toluene is then added dropwise at the same temperature during the course of 30 minutes and whilst introducing nitrogen and the mixture is stirred for a further 8 hours. The reaction mixture

is then poured into 1000 cc of water, the toluene layer is separated and the aqueous phase is shaken out a further three times with toluene. The combined organic solutions are then washed three times with 2N sodium carbonate solution and twice with water, dried over magnesium sulphate and the solvent is evaporated at reduced pressure. The residue is distilled in a high vacuum, whereby 6-methoxy-9,10-dihydro-4H-benzo[4,5]cyclohepta[1,2-b]thiophen-4-one distils at 165—180°/0.1—0.5 mm Hg. It is worked up further as such without additional purification.

The 5 - methoxy - 2[2 - (2 - thienyl)-ethyl] - benzoic acid used as starting material is produced as follows:

5-methoxy-phthalaldehydic acid.

A mixture of 20.5 g of 6-methoxy-phthalide, 20.5 g of N-bromosuccinimide and 0.06 g of dibenzoyl peroxide in 1000 cc of anhydrous carbon tetrachloride is heated to the boil for 22 hours whilst stirring. The solution is filtered whilst hot and the solvent is evaporated at 15 mm Hg. The crude 3-bromo-6-methoxy-phthalide is then heated at reflux for 4 hours together with 500 cc of water, the resulting hot solution is filtered through highly purified diatomaceous earth and the filtrate is cooled. The precipitated acid is filtered off and the mother liquor is concentrated to half its volume, whereupon a further portion of acid is filtered off. After drying in a high vacuum at 60° the acid melts at 142—143°.

5 - methoxy - 2 - [2 - (2 - thienyl) - vinyl] - benzoic acid.

1 to 2 cc of a solution of 40.0 g of 5-methoxy-phthalaldehydic acid and 52.0 g of 2-thienyl-diethyl-phosphonate in 80 cc of dimethyl formamide are added dropwise to a suspension of 26.6 g of sodium methylate in 80 cc of dimethyl formamide, whereby the temperature of the mixture rises to 30°. The flask is then placed in an ice bath and the entire solution of 5-methoxy-phthalaldehydic acid and 2-thienyl-diethyl-phosphonate in 80 cc of dimethyl formamide is added dropwise as rapidly as possible, at such a rate that the internal temperature remains at 30—35°. The mixture is then stirred for a further 30 minutes at room temperature. 2500 cc of water are added to the reaction solution at 10—15° whilst cooling well and the aqueous solution is shaken out with 150 cc of benzene. The aqueous solution is then carefully adjusted to a pH value of 3 to 4 at 5—10° with 2N hydrochloric acid. After 2 to 3 hours the precipitated acid is filtered off and recrystallized from benzene. Melting point 170—171°.

5 - methoxy - 2 - [2 - (2 - thienyl) - ethyl] - benzoic acid.

19.0 g of sodium are melted with anhydrous toluene, whereupon 1250 g of pure mercury are added dropwise whilst stirring frequently at such a rate that the toluene boils. The mixture is then heated to 120—140° whilst stirring and as soon as all the toluene is evaporated cooling is effected to 60°. A solution of 49.0 g of 5-methoxy-2-[2-(2-thienyl)-vinyl]-benzoic acid in 400 cc of 95% ethanol is poured into the homogeneous amalgam and the mixture is vigorously stirred for 90 minutes. The mercury is then separated, washed three times with ethanol and the combined ethanolic solutions are diluted with 3000 cc of water. The solution is filtered through highly purified diatomaceous earth and slowly adjusted to a pH value of 1 with 2N hydrochloric acid whilst stirring. After a number of hours the precipitated acid is filtered off and crystallized from chloroform/hexane. Melting point 120—122°.

EXAMPLE 5:

25 7 - chloro - 4H - benzo[4,5]cyclohepta[1,2-b]thiophen - 4 - one.

A mixture of 24.8 g of 7-chloro-9,10-dihydro - 4H - benzo[4,5]cyclohepta[1,2-b]thiophen - 4 - one (production see Example 2), 17.8 g of N-bromosuccinimide and 50 mg of dibenzoyl peroxide in 2500 cc of absolute carbon tetrachloride is heated to 100° for 22 hours whilst stirring. The reaction mixture is left to cool, filtration is effected and the filtrate is evaporated to dryness at 50° and reduced pressure. The residue is dissolved in 250 cc of triethylamine and the solution is heated to the boil at reflux for 2 hours. The reaction mixture is then evaporated to dryness at reduced pressure and the residue taken up in 200 cc of 2N hydrochloric acid. Extraction is effected a number of times with methylene chloride, the combined extracts are washed with water until neutral, dried over sodium sulphate and evaporated to dryness. For purposes of purification the crude product is recrystallized twice from acetone and once from ethanol. Pure 7 - chloro - 4H - benzo[4,5]cyclohepta[1,2-b]thiophen - 4 - one melts at 141—142°.

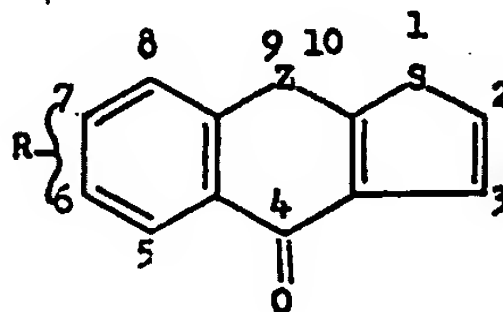
EXAMPLE 6:

6 - chloro - 4H - benzo[4,5]cyclohepta[1,2-b]thiophen - 4 - one.

The above mentioned compound is produced from 6-chloro-9,10-dihydro-4H-benzo[4,5]cyclohepta[1,2-b]thiophen - 4 - one (see Example 1) by dehydrogenating in a manner analogous to that described in Example 5. Upon recrystallization from benzene, the compound melts at 152—153°C.

WHAT WE CLAIM IS:—

1. A process for the production of 4H-benzo[4,5]cyclohepta[1,2-b]thiophen - 4 - one derivatives of the general formula:

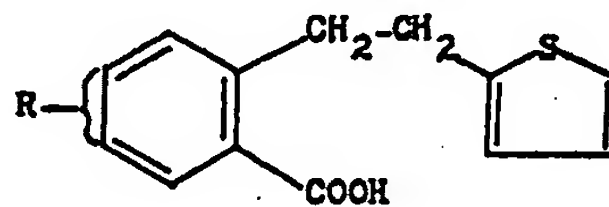


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I

in which R signifies a chlorine or bromine atom or an alkoxy radical of 1 to 4 carbon atoms inclusive, and Z signifies the radical —CH=CH— or —CH₂—CH₂—, characterized in that a 2-[2-(2-thienyl)-ethyl]-benzoic acid of the general formula

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II

in which R has the above significance, is cyclized by treatment with polyphosphoric acid and the resulting compound I in which Z signifies the radical —CH₂—CH₂— is dehydrogenated in the 9,10-position, when an unsaturated compound of formula I is required, by treatment with a halogenating agent followed by dehydro-halogenation.

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2. A process for the production of the compounds of the general formula I stated in Claim 1 substantially as herein described with reference to any one of the Examples.

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3. Compounds of the general formula I stated in Claim 1 whenever produced by a process as claimed in either one of Claims 1 and 2.

4. Compounds of the general formula I stated in claim 1.

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5. 6 - chloro - 9,10 - dihydro - 4H - benzo[4,5]cyclohepta[1,2-b]thiophen - 4 - one.

6. 7 - chloro - 9,10 - dihydro - 4H - benzo[4,5]cyclohepta[1,2-b]thiophen - 4 - one.

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7. 6 - bromo - 9,10 - dihydro - 4H - benzo[4,5]cyclohepta[1,2-b]thiophen - 4 - one.

8. 6 - methoxy - 9,10 - dihydro - 4H - benzo[4,5]cyclohepta[1,2-b]thiophen - 4 - one.

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9. 7 - chloro - 4H - benzo[4,5]cyclohepta[1,2-b]thiophen - 4 - one.

10. 6 - chloro - 4H - benzo[4,5]cyclohepta[1,2-b]thiophen - 4 - one.

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